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13. ABSTRACT (Maximum 200 words) This project addressed the development of a new class of metal/organic supramolecular polymers, which are prepared by the self-assembly of ditopic ligands and appropriate metal ions. The ditopic ligand consists of two 2,6-bis(1'-methyl-benzimidazolyl)pyridine ligands, which are connected to each other by either a conjugated poly(<i>p</i> -phenylene ethynylene) (PPE) core or a poly(<i>p</i> -xylyene) (PPX) core. The metal/organic supramolecular polymers based on ditopic poly(<i>p</i> -xylyene) macromonomers were investigated as easy-to-process high-temperature-resistant materials. We demonstrated that these supramolecular materials are indeed easily processably in common organic solvents and that their thermal stability is very similar to that of common (but intractable) poly(<i>p</i> -xylenes). In addition, investigations of metallo-supramolecular polymers based on the ditopic poly(<i>p</i> -phenylene ethynylene) macromonomers have demonstrated the potential of these systems as sensors for chemical warfare agents. In particular, we have shown that these materials and selected derivatives exhibit significant changes in fluorescence in the presence of organophosphates and that different organophosphates show different responses.				
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Enclosure 1

High Temperature Resistant Organic/Inorganic Hybrid Polymers: An Architectural Study

DAAD19-03-1-0208

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Knapton, D.; Iyer, P.; Rowan, S.J.; Weder C. Synthesis and properties of metallo-supramolecular poly(*p*-xylylene)s. *Macromolecules* **2006**, 39 (12), 4069-4075.

Knapton, D.; Rowan, S.J.; Weder, C.; Metallosupramolecular Conjugated Polymers; *Polym. Mater. Sci. Eng. Prepr.* **2006**, 95.

Burnworth, M.; Knapton, D.; Rowan, S.J.; Weder, C.; Fluorescent Organometallic Sensors for the Detection of Chemical Warfare Agent Mimics; *Polym. Mater. Sci. Eng. Prepr.* **2006**, 95.

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- (h) Number of FTE Grad Students supported by this agreement: 0
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A. Investigation into the Use of Metallo-Supramolecular Polymers as Processable High Temperature Materials

Introduction:

In our efforts to develop high-temperature-stable organic/inorganic hybrid polymers, we embarked on the exploration of a new class of metallo-supramolecular polymers. The molecular design utilized in the present study merges the chemical structure of poly(arylene alkylene)s,¹ which offer outstanding thermal and mechanical properties, with the inherent processing advantages of dynamic (reversible) polymerization.² Poly(*p*-xylylene) (PPX)³ is the most prominent representative of the poly(arylene alkylene) family. This polymer and its derivatives are well-known for an appealing combination of high thermal stability excellent solvent resistance, high degree of crystallinity, low dielectric permittivity and outstanding barrier properties^{4,5} In addition, PPX exhibits excellent mechanical properties with a Young's Modulus and tensile strength of ca. 2.4 GPa and ca. 47 MPa respectively.⁴ Thus, PPX is an attractive material for many applications, including packaging of electronic components, medical device fabrication, and artifact conservation.⁴ Unfortunately, broad industrial exploitation of PPX is stifled by the obstacles which the material presents to conventional processing technologies.⁶ The high melting temperature of PPX (424 °C) is from an application point of view highly attractive, but it overlaps with the onset of thermal degradation, which prevents the melt-processing of PPX.⁷ In addition PPX displays, even at elevated temperatures, a very low solubility in nearly all common solvents, thus thwarting solution-based processing options.⁶ As a result, the only practical approach for the synthesis and processing of PPX is by chemical vapor deposition⁸ (CVD) polymerization, which involves the vapor phase pyrolysis of [2.2]paracyclophanes,⁹ diesters of α,α' -dihydroxy-*p*-xylenes,¹⁰ or α -bromo-*p*-xylenes¹¹ and the subsequent polymerization of the resulting 1,4-quinodimethanes upon deposition on a cold substrate.¹² Several alternative approaches to prepare PPX derivatives or PPX-analogous polymers with an enhanced processability have been proposed, involving the increase of the number of methylene groups comprised in the polymer backbone,^{1,13} as well as the introduction of solubilizing side chains.^{11,14,15} Unfortunately, most of these polymers, when compared to the original PPX, exhibit a dramatically reduced crystallinity – some materials are fully amorphous – and show low melting or glass transition temperatures, and, thus, have largely failed to substitute PPX in practical applications. Our research supported by this grant has shown that this dilemma can, in part, be solved by utilizing a supramolecular polymerization process, as it allows for the assembly of high-molecular-weight polymeric aggregates from well-defined, easy-to-process precursors.² As several recent studies have demonstrated, a variety of non-covalent interactions can be utilized to assemble a wealth of different monomers.^{2b,c} One particularly useful and well-studied means of preparing supramolecular polymers is the utilization of metal-ligand interactions (**Figure 1**).¹⁶⁻²⁰ A wide variety of metal-ligand binding motifs is available that offer a broad range of binding characteristics (e.g. thermodynamic and kinetic stabilities),²¹ which in turn can be utilized to tune the nature of the resulting supramolecular materials.²²

Results:

Development of Synthetic Framework. We successfully developed synthetic protocols for the synthesis of the desired PPE and PPX ditopic monomers, in which the key steps are the Sonogashira coupling of 2,5-dioctyloxy-1,4-diiodo benzene²³ with the new 2,6-bis(1'-methyl-benzimidazolyl)-4-ethynyl-pyridine, which affords **1a** in good yield, and the subsequent reduction of the ethynyl bonds using Hahn diimide reduction chemistry resulting in **2a** (**Figure 2**). The polymeric equivalents of **1a** and **2a** were also prepared via this framework: 2,6-bis(1'-methylbenzimidazolyl)pyridine (**Mebip**) end-capped poly(2,5-dioctyloxy-*p*-phenylene ethynylene) macromonomer (**1b**) was prepared via the cross-coupling reaction of aryl bisiodide and 2,5-dioctyloxy-1,4-ethynyl benzene, using Mebip 2,6-bis(1'-methylbenzimidazolyl)-4-ethynylpyridine as an end-capper (**Figure 2**). In view of the limited solubility of high-molecular-weight PPEs with octyloxy side chains,²³ the number-average degree of polymerization, X_n , was controlled to a target value of 20 by slightly off-setting the ratio of the two bifunctional monomers. According to standard procedure,²³ the polycondensation reaction was performed using Pd(PPh₃)₄/CuI as catalyst system in a mixture of toluene/diisopropylamine.

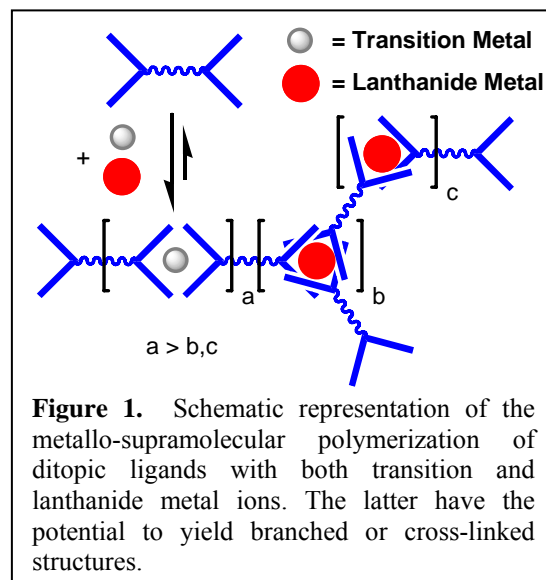


Figure 1. Schematic representation of the metallo-supramolecular polymerization of ditopic ligands with both transition and lanthanide metal ions. The latter have the potential to yield branched or cross-linked structures.

The procedure for purification and isolation of macromonomer **1** varied significantly from that of normal PPEs. In order to ensure removal of any Mebip binding Pd and Cu residues the polymerization reaction mixture was stirred for an extended period over a saturated aqueous solution of EDTA and subsequently extensively extracted with a battery of solvents. Macromonomer **1b**, which was completely soluble in solvents such as CHCl₃, toluene and THF was characterized by ¹H and ¹³C NMR spectroscopy. As in earlier studies,²³ the number-average degree of polymerization, X_n , of ≈ 27 determined by ¹H NMR end group analysis was slightly higher than targeted (20), consistent with the loss of low-molecular weight material during the reaction workup, which is evident from the color of the filtrates obtained following precipitation.²⁴

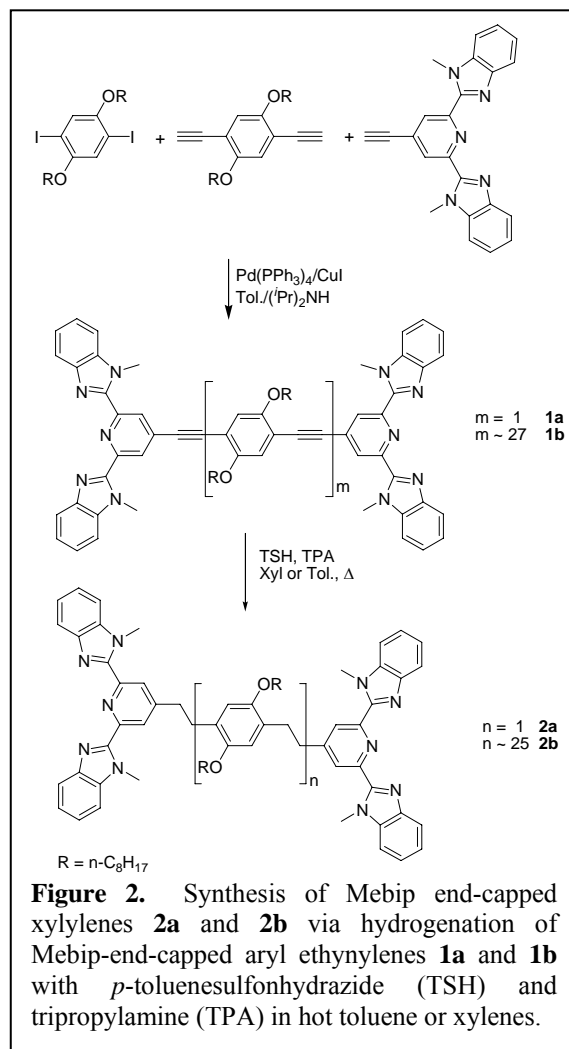
2,6-Bis(1'-methylbenzimidazolyl) pyridine end-capped 2,5-dialkoxy-*p*-xylylene macromonomers **2b** were prepared via the Hahn diimide reduction of their respective conjugated species **1b**. Extensive purification via repeated precipitation from MeOH yielded the desired compounds, the identity of which was confirmed by ¹H, ¹³C NMR and MALDI-TOF MS. Optical characterization by UV/vis spectroscopy revealed the absence of the π - π^* transition related to the conjugated ethynyl backbone. In addition, the spectrum reveals a strong absorption band centered around 320 nm that can be attributed to the π - π^* transition of the Mebip moiety.

Optical Properties of Macromonomer 1b. With reference to the potential usefulness in optical applications, the photophysical characteristics of the conjugated macromonomer **1b** were investigated in both CHCl₃ solution and spin-cast thin films; all spectroscopic data are summarized in Table 1 and absorption and emission spectra are shown in **Figure 3**. The solution spectrum exhibits a main absorption band centered at 448 nm and a weaker band around 319 nm. These transitions are associated with the π - π^* and n - π^* transition of the polymer backbone, respectively. Optical excitation of **1b** causes intense photoluminescence. The emission spectrum displays two well-resolved bands near 480 and 511 nm and exhibits features that are consistent with π - π^* fluorescence. A comparison between these optical data of **1b** and poly(2,5-dioctyloxy-*p*-phenylene ethynylene) without the Mebip endgroups²³ reveals that these materials display virtually identical optical characteristics, indicating that the Mebip endgroups do not alter the electronic properties of the PPE backbone. Homogeneous films of good optical quality could be produced by spin-coating. The absorption spectrum of a spin-cast film of macromonomer **1b** shows a slight red-shift when compared to solution (the transitions observed in solution at 448 and 319 nm now appear around 455 and 320 nm, and displays a new sharp feature at 485 nm (**Figure 3b**). The solid-state PL emission spectrum is significantly red-shifted and broadened. These features are characteristic of PPE aggregation and pronounced intermolecular interactions.^{23,25,26} It should be noted that the detailed features of the solid-state spectra are related to the degree of order, which is dependent of and can be controlled by the processing conditions.

Table 1. Optical absorption and PL emission data of macromonomer **1b** and supramolecular polymers based on equimolar amounts of **1b** and Zn²⁺ or Fe²⁺ ions.

	Solution (CHCl ₃)		Thin Film	
	Absorption λ_{\max} (nm)	Emission λ_{\max} ^a (nm)	Absorption λ_{\max} (nm)	Emission λ_{\max} ^a (nm)
1b	319, 448	480, 510	320, 455, 485	543, 580
1b ·Zn(ClO ₄) ₂	n.a. ^c	480, 665 ^d	321, 453, 485	670
1b ·Fe(ClO ₄) ₂	n.a. ^c	n.a.	320, 444, 476, 635	- ^b

^aExcitation at 400 nm. ^bEmission is fully quenched. ^cNot available due to the high extinction of concentrated solutions which display adequate binding. ^d1.86 mg/mL.



Self-Assembly and Solution Properties of the Metallo-Supramolecular Polymers of **1b**.

We demonstrated that the formation of metallo-supramolecular polymers of the type $[\mathbf{1b} \cdot \text{MX}_2]_n$ is readily achieved by the addition of one equivalent of metal ion salt dissolved in CH_3CN to a CHCl_3 solution of macromonomer **1b**. We found that a variety of metals, including Co^{2+} , Ni^{2+} and Cd^{2+} display appropriate interactions (i.e., large equilibrium constant and rapid complexation kinetics) that allow for supramolecular polymerization utilizing the terdentate MeBIP motif.²⁴ We studied complexes with Zn^{2+} and Fe^{2+} in detail, with the intent to probe the influence of the different electronic characteristics of these metals on the resulting metallopolymer. Zn^{2+} features a fully occupied d-orbital ($3d^{10}$) and is a prototype for metals that show hardly any tendency for metal-to-ligand charge transfer (MLCT) with imine ligands.²⁷ In a variety of different systems, we previously observed orange PL from Zn-imine complexes,^{24,28} and we speculated that this feature might be useful to tune the emission characteristics of the materials investigated here. By contrast, Fe^{2+} is well known for to form pronounced MLCT complexes and to act as a strong fluorescence quencher. A 1:1 Binding ratio of macromonomer **1b** with both these metals leads to pronounced visual changes; A stoichiometric amount of Zn^{2+} in CH_3CN relative to the number of MeBIP units present plus a small 4% excess of Zn^{2+} to ensure full complexation was added to an orange solution of **1b** in CHCl_3 (38.5 mg/mL) resulting in the instantaneous formation of a red mixture with a significant increase in the solution's viscosity.²⁹ The slight excess of Zn^{2+} was not expected to interfere with the self-assembly process as similar MeBIP endcapped systems exhibit cooperative behavior. It should also be noted that the high concentration of **1b** used in the preparation of the supramolecular polymers was employed to ensure that the maximum molecular weight was achieved. That is, the molecular weight of supramolecular systems can be roughly estimated according to the Multi-Stage Open Association Model which predicts that the degree of polymerization (DP) is proportional to the square root of the total concentration of components present. Evaporation of the solvent led to a red solid, which displayed appreciable mechanical properties. This metallopolymer could be re-dissolved in CHCl_3 ³⁰ and the resulting solutions were employed to (i) produce thin films for optical experiments by spin-coating, free-standing films (thickness ca. 60 μm) for mechanical experiments by solution-casting, and monofilaments by a simple solution-spinning technique. These samples, shown in **Figure 4**, visualize unequivocally that $[\mathbf{1b} \cdot \text{Zn}(\text{ClO}_4)_4]_n$ – very much in contrast to the neat macromonomer **1b** and a poly(2,5-dioctyloxy-*p*-phenylene ethynylene) of similar DP but without the Bip endgroups – offers considerable mechanical strength and flexibility. Metallopolymer based on **1b** and Fe^{2+} were prepared in similar fashion; in this case, a stoichiometric amount of Fe^{2+} in CH_3CN relative to the number of MeBIP units present plus a small 4% excess of Fe^{2+} to ensure full complexation was added to an orange solution **1b** in CHCl_3 (38 mg/mL) led to the instantaneous

formation of a green mixture and a significant increase of the solution's viscosity. Here, the solution was directly processed into thin films for optical experiments by spin-coating and free-standing films (thickness ca 110 μm) for mechanical experiments by solution-casting.

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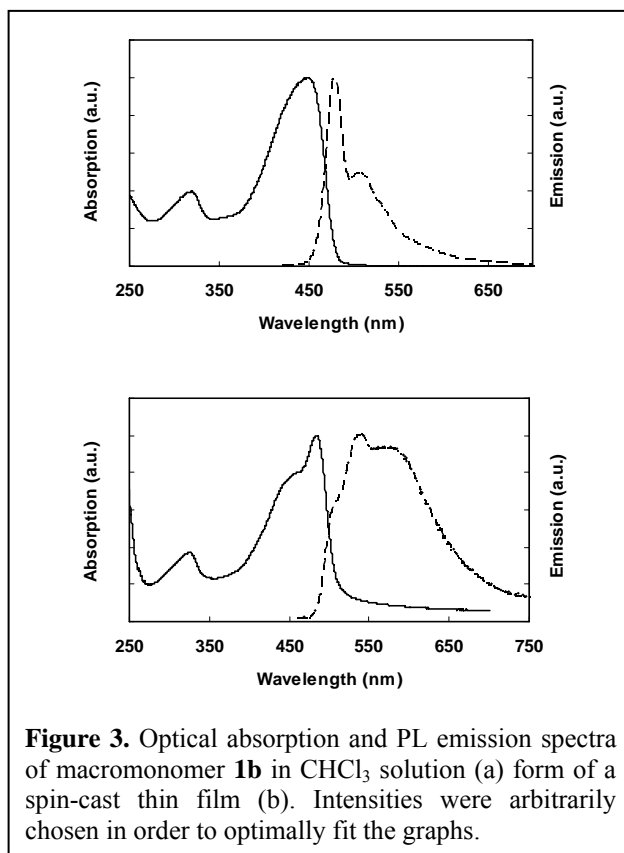


Figure 3. Optical absorption and PL emission spectra of macromonomer **1b** in CHCl_3 solution (a) form of a spin-cast thin film (b). Intensities were arbitrarily chosen in order to optimally fit the graphs.

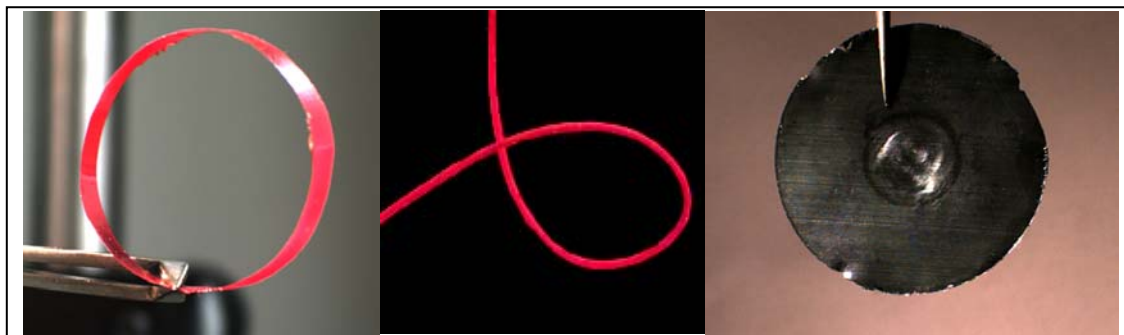


Figure 4. A film and fiber (shown under illumination with UV light) based on metallo-supramolecular polymer $[\mathbf{1b} \cdot \text{Zn}(\text{ClO}_4)_2]_n$, and a film comprised of metallo-supramolecular polymer $[\mathbf{1b} \cdot \text{Fe}(\text{ClO}_4)_2]_n$ (left-to-right).

Optical Properties of $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$ and $[\mathbf{1b}\cdot\text{Fe}(\text{ClO}_4)_2]_n$. Solid-state optical absorption and PL emission spectra of $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$ were measured on thin films that were prepared by spin-casting from CHCl_3 solutions of approximately 1.0 mg/mL of polymer. The absorption spectrum (**Figure 5**) exhibits essentially the same features as a thin film of the neat macromonomer **1b**, i.e., broad bands around 453 and 321 nm and a narrow aggregation band at 484 nm. The contribution of the aggregation band is more pronounced than in **1b**, which appears to indicate a higher degree of long-range structural order for the metallopolymer (vide infra). Other than that, the similarity of the absorption spectra of **1b** and $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$ suggests that the bandgap of the conjugated PPE sequences remains essentially unchanged upon binding of **1b** with Zn^{2+} . PL spectra of solutions approximately double the concentration of those used for spin casting (1.86 mg/mL) and thin films are identical and reveal that the emission associated with the PPE moieties is nearly completely absent in case of $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$. Instead, the spectra of both thin films and concentrated solution display a very weak, broad emission band around 665 nm, which is also reflected by the material's weak orange-red glow upon illumination with UV light (**Figure 4**). Rather interestingly, excitation spectra (not shown) link this emission to an electronic transition that can be best excited around 540 nm, but is not discernible in the material's absorption spectrum. Excitation experiments further reveal that optical excitation of the PPE moieties under dilute conditions leads to relaxation by non-emissive pathways, while weak energy transfer to the red-emitting excited state is observed in thin films and concentrated solutions. With the goal of attaining further insight into the mechanism of the Zn^{2+} -mediated self-assembly process of **1b**, we titrated $\text{Zn}(\text{ClO}_4)_2$ into a solution of **1b** and examined the resulting products by means of PL spectroscopy. It should be noted that the precipitation of high molecular weight macromolecules at increased concentrations dictated that the PL titration experiment be performed at rather low concentrations (22 μM). As such, these conditions clearly favor the formation of oligomeric species as opposed to high molecular weight aggregates. **Figure 6** reveals that the emission associated with the PPE moieties is strongly quenched upon addition of Zn^{2+} . The effect depends on the concentration of Zn^{2+} in a nonlinear fashion and levels off at a $\text{Zn}^{2+}:\mathbf{1b}$ ratio of 1. At this point the emission observed for the neat **1b** is almost completely quenched; **Figure 6** also reveals some weak remaining emission that is characteristic of **1b**, and appears to reflect that under the (dilute) conditions of this titration experiment, a small fraction of the macromonomer remains unbound. Quite interestingly, the intensity of the aforementioned red emission band centered around 665 nm increased with increasing concentration of Zn^{2+} to display a maximum intensity at a $\text{Zn}^{2+}:\mathbf{1b}$ ratio of 1, before losing intensity at higher $\text{Zn}^{2+}:\mathbf{1b}$ ratios. Thus, the data suggest the formation of a metallo-supramolecular complex of the form $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$, in which each Mebip ligand is bound to a Zn^{2+} ion. The resulting Mebip[Zn]Mebip moieties, somewhat unexpectedly, appear to represent non-emissive sites to which the excitation of the PPE moieties is directed via energy transfer processes. **Figure 6** reveals that in dilute solution the relative contribution of the red emission band is indeed very low, but a comparison with the emission spectra obtained under more concentrated conditions reveals that its relative magnitude (to that of uncomplexed **1b**) increases with increasing concentration of $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$. While the exact origin of the emission is at this point unidentified, the current

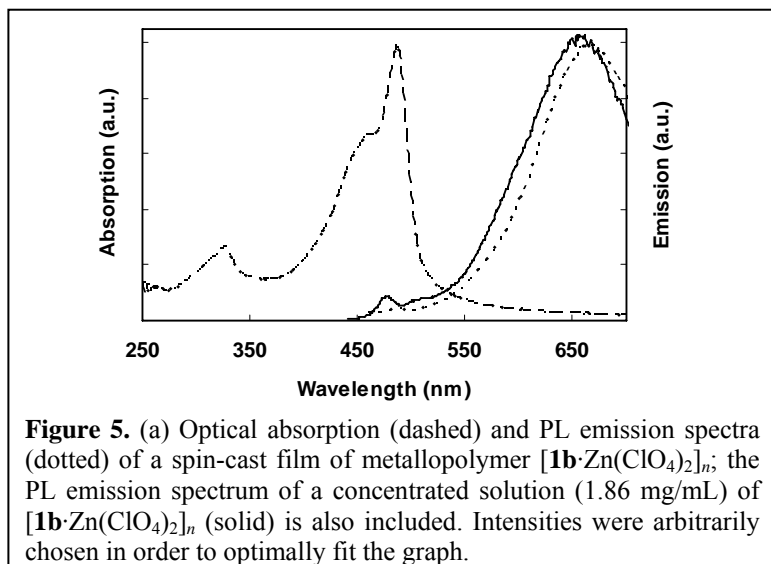


Figure 5. (a) Optical absorption (dashed) and PL emission spectra (dotted) of a spin-cast film of metallopolymer $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$; the PL emission spectrum of a concentrated solution (1.86 mg/mL) of $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$ (solid) is also included. Intensities were arbitrarily chosen in order to optimally fit the graph.

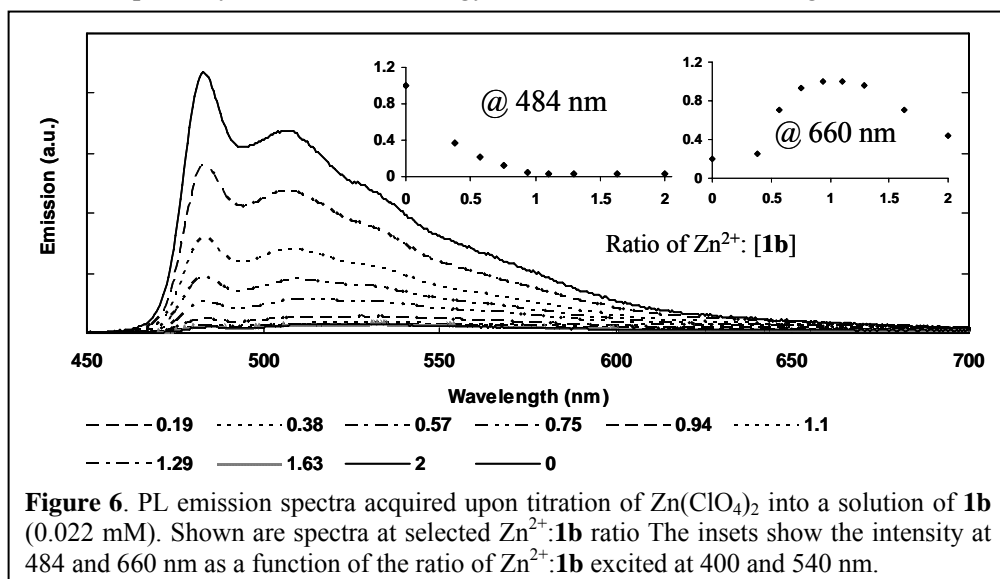
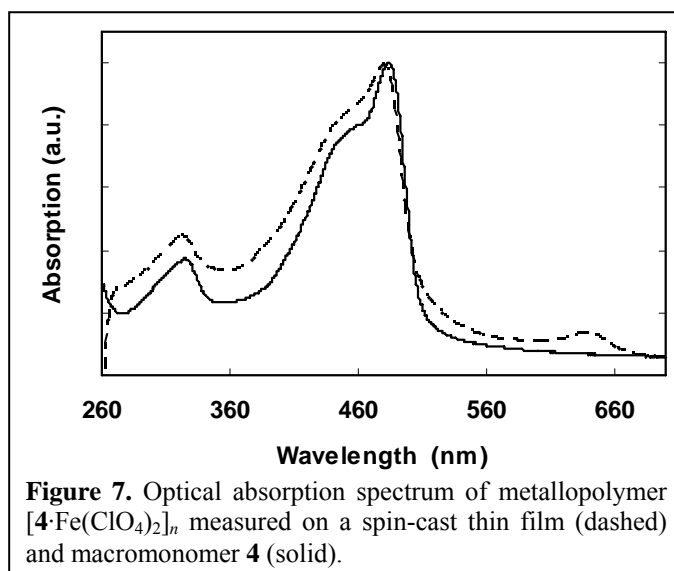


Figure 6. PL emission spectra acquired upon titration of $\text{Zn}(\text{ClO}_4)_2$ into a solution of **1b** (0.022 mM). Shown are spectra at selected $\text{Zn}^{2+}:\mathbf{1b}$ ratio. The insets show the intensity at 484 and 660 nm as a function of the ratio of $\text{Zn}^{2+}:\mathbf{1b}$ excited at 400 and 540 nm.

observations suggest a forbidden (weak) transition that is related to the Mebip[Zn]Mebip moieties. The addition of Fe^{2+} to macromonomer **1b** causes, not unexpectedly, rather different optical changes than Zn^{2+} . The absorption spectrum (**Figure 7**) exhibits essentially the same features as a thin film of the neat macromonomer **1b**, i.e., broad bands around 445 and 320 nm and a narrow aggregation band at 476 nm. In addition, a characteristic metal-to-ligand charge transfer absorption band centered at 635 nm can be observed, which is indicative of the formation of the 2:1 Mebip: Fe^{2+} complex, as it is required for the formation of the supramolecular polymer. The addition of Fe^{2+} , unlike Zn^{2+} , expectedly resulted in the complete quenching of the solid state fluorescence.



Thermomechanical Properties of $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_4]_n$ and $[\mathbf{1b}\cdot\text{Fe}(\text{ClO}_4)_4]_n$. The thermal and mechanical properties of the $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_4]_n$ and $[\mathbf{1b}\cdot\text{Fe}(\text{ClO}_4)_4]_n$ supramolecular polymers and the parent macromonomer **1b** were investigated by means of thermogravimetric analysis (TGA) and dynamic mechanical thermoanalysis (DMTA). TGA traces (**Figure 8**) acquired under Nitrogen atmosphere suggest that the neat **1b** is stable up to a temperature of 363 °C, where a weight loss of 2 % is observed. However, it should be noted that thermal cross-linking of the ethynylene units is a common pathway for the decomposition of poly(*p*-2,5-dialkoxy phenylene ethynylene)s;³¹ this reaction, which cannot be discerned by TGA, typically occurs at temperatures above 150 °C. The TGAs show that both the Zn and Fe polymers exhibit a 2 % weight-loss at lower temperatures than the uncomplexed macromonomer (313 and 250 °C respectively), most likely corresponding to the thermal degradation of the perchlorate anion. Both polymers ($[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_4]_n$ in particular), however, appear to be stable in the temperature regime tolerated by the conjugated PPE building blocks, i.e., up to ca. 150 °C. It is also important to note that the self-assembly process does not significantly alter the thermal properties of macromonomer **1b**.

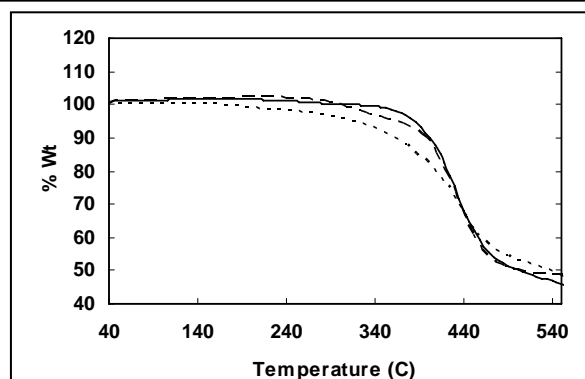


Figure 8. Thermo gravimetric analysis traces of **1b** (solid), $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$ (dashed) and $[\mathbf{1b}\cdot\text{Fe}(\text{ClO}_4)_2]_n$ (dotted). Experiments were conducted under N_2 at a heating rate of 20 °/min.

Gratifyingly, both $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_4]_n$ and $[\mathbf{1b}\cdot\text{Fe}(\text{ClO}_4)_4]_n$ films displayed sufficient mechanical strength to allow for characterization by dynamic mechanical thermo analysis (DMTA,) (**Figure 9**). Experiments were conducted in a temperature range of -20 to 100 °C. The moduli of $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_4]_n$ and $[\mathbf{1b}\cdot\text{Fe}(\text{ClO}_4)_4]_n$ were determined to be ca 159 and ca 138 MPa at -20 °C and ≈ 100 and ≈ 83 MPa at 25 °C respectively. A decrease in the modulus of both films was observed over the experimental temperature range; $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_4]_n$ exhibits a distinguishable transition at approximately 40 °C, which in view of the striking similarity to the trace of a high-molecular poly(*p*-2,5-dialkoxy phenylene ethynylene) ($M_n \sim 83,000$ g mol⁻¹ reported before,³¹ we tentatively assign to a glass transition. While the moduli of $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_4]_n$ and $[\mathbf{1b}\cdot\text{Fe}(\text{ClO}_4)_4]_n$ appear to be slightly lower than the one of a high-molecular poly(*p*-2,5-dialkoxy phenylene ethynylene) reported before,³¹ they appear to be the first ever reported for any metallo supramolecular conjugated polymer.

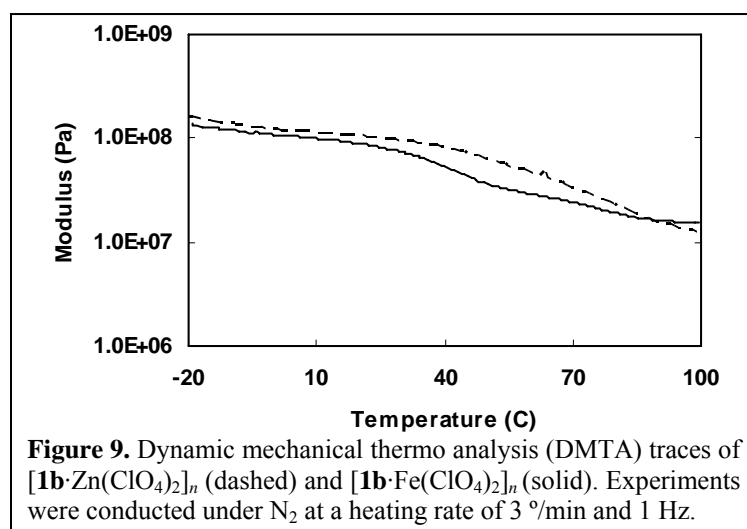


Figure 9. Dynamic mechanical thermo analysis (DMTA) traces of $[\mathbf{1b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$ (dashed) and $[\mathbf{1b}\cdot\text{Fe}(\text{ClO}_4)_2]_n$ (solid). Experiments were conducted under N_2 at a heating rate of 3 °/min and 1 Hz.

Self-Assembly and Solution Properties of the Metallo-Supramolecular Polymers of 2a and 2b. The formation of metallo-supramolecular species $[\mathbf{2a}\cdot\text{MX}_n]_n$ and $[\mathbf{2b}\cdot\text{MX}_n]_n$ is readily achieved by the addition of one equivalent of the desired metal ion salt to a solution of the Mebip end-capped xylylenes **2a** and **2b**. We found that a variety of metal ions

display appropriate interactions (i.e., large equilibrium constants and rapid complexation kinetics) and allow for supramolecular polymerization using the terdentate Mebip motif.²⁴ Encouraged by the successful metallopolymerization of Mebip-endcapped PPEs with Zn^{2+} and Fe^{2+} ,^{24b} we opted to employ these metal ions in the present study. In order to probe the complexation characteristics of **2a** and **2b**, we first conducted a detailed optical titration study with Zn^{2+} , which offers both a large equilibrium constant and rapid complexation kinetics. To this end, $\text{Zn}(\text{ClO}_4)_2$ was titrated into solutions of **2a** and **2b**, and the resulting products were analyzed by means of UV-vis spectroscopy (**Figure 10**). It should be noted that precipitation, presumably of high-molecular weight macromolecules, was observed when these experiments were carried out at too high concentrations; this dictated that the UV-vis titrations be performed at a concentration of 22–25 μM of the respective ditopic ligands. As such, these conditions clearly favor the

formation of oligomeric species as opposed to high-molecular-weight aggregates. The addition of Zn^{2+} to xylylenes **2a** and **2b** rendered the originally colorless solutions pale yellow. In both cases a new lowest-energy absorption band was observed, centered at 354 nm in the case of **2a** and 360 nm in the case of **2b** (**Figure 10**). Concomitantly, in model compound **2a** the intensity of the initial absorption band with λ_{max} at 318 nm associated with the $\pi-\pi^*$ transition of the Mebip moiety was significantly reduced upon binding, as was the related absorption of macromonomer **2b** observed as a shoulder at ~ 330 nm. The spectra of both titration series exhibit a single isosbestic point at ~ 340 nm up to a $\text{Zn}^{2+}:\text{2}$ ratio of approximately one suggesting equilibria between the bound and unbound monomers **2a** and **2b**. At $\text{Zn}^{2+}:\text{2}$ ratios greater than one, new isosbestic points are observed, which appear to correspond to the presence of chain-terminating monomer- Zn^{2+} -solvent complexes formed upon depolymerization of the supramolecular species in the presence of an excess of metal.^{24a} We further quantified the spectral changes observed in the above-discussed Zn^{2+} titrations as the normalized intensity of the emerging absorption bands; the data are plotted in the insets of **Figure 10**. Gratifyingly, the changes are virtually identical for the well-defined mono-disperse model compound **2a** and the macromonomer **2b**, leveling off at a $\text{Zn}^{2+}:\text{2}$ ratio of 1:1, which is consistent with the ditopic nature of the monomers and the successful self-assembly in dilute solution. Similar titration data were obtained upon addition of $\text{Fe}(\text{ClO}_4)_2$ to **2b**. In this case, a characteristic^{24,32} metal-to-ligand charge transfer absorption band was observed at 570 nm.

Preparation and Solid-State Properties of Metallo-Supramolecular Polymers based on 2b. Monomer **2b** is a pale yellow powder, which is soluble in chloroform and can readily be spin- or solution-cast into homogeneous thin films. However, these films do not display self-supporting mechanical properties. The preparation and processing of metallo-supramolecular polymers based on **2b** and $\text{Zn}(\text{ClO}_4)_2$ or $\text{Fe}(\text{ClO}_4)_2$ ($[\text{2b}\cdot\text{M}]_n$) followed the protocol developed for similar materials comprising a Mebip-end-capped poly(2,5-dialkyloxy-*p*-phenylene ethynylene) **1b** of an number-average degree of polymerization (X_n) similar to that of **2b**,²⁴ which display outstanding mechanical properties (**Figure 11**). The procedure involved co-dissolution of **2b** and an equimolar amount of either of the metal salts in a $\text{CHCl}_3/\text{CH}_3\text{CN}$ mixture, followed by solution casting. The addition of either $\text{Zn}(\text{ClO}_4)_2$ or $\text{Fe}(\text{ClO}_4)_2$ in CH_3CN to **2b** in CHCl_3 resulted in solutions of $[\text{2b}\cdot\text{Zn}(\text{ClO}_4)_2]_n$ and $[\text{2b}\cdot\text{Fe}(\text{ClO}_4)_2]_n$, which upon casting and drying yielded films that displayed poor mechanical properties (**Figure 11**). In order to probe if an increase of the X_n of the macromonomer would change this situation, the experiment was repeated with a macromonomer **2b** of an X_n of ~ 32 , but the behavior of this ditopic ligand was virtually the same.

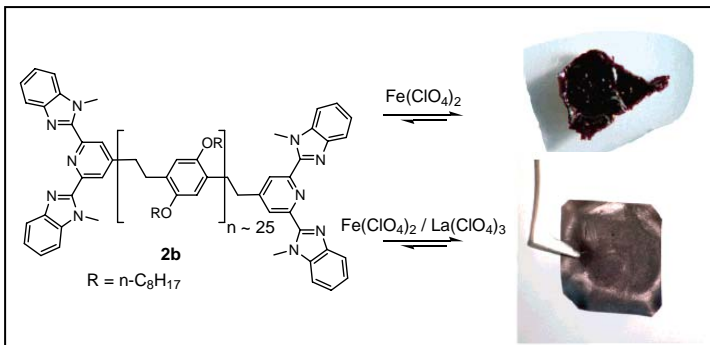
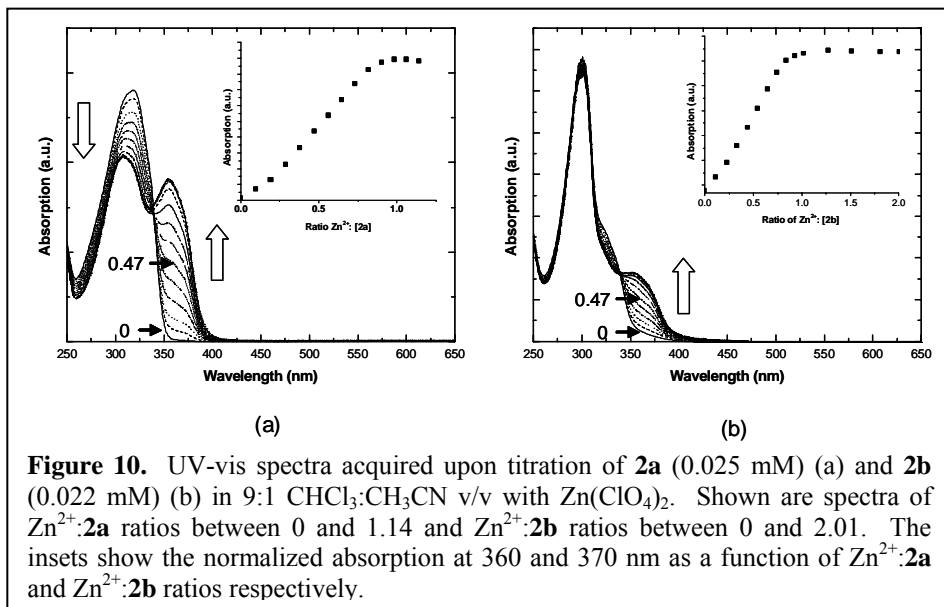


Figure 11. Chemical structures of Mebip end-capped poly(2,5-dioctyloxy-*p*-xylylene) (PPX) (**3b**) which forms MSPs upon addition of appropriate metal salts and pictures of the resulting films prepared by solution casting.

Thus, the $[2b \cdot M]_n$ samples investigated here display mechanical properties that are clearly inferior when compared with the corresponding $[1b \cdot M]_n$ analogues. The structural purity of **2b** established by NMR, the successful self-assembly in dilute solution established by optical titration, and the fact that the binding strength of **2b** should be similar to that of **1b** and many related systems, suggests that the $[2b \cdot M]_n$ supramolecular materials prepared here are indeed of polymeric nature. Thus, the observation of poor mechanical properties seems to reflect the lack or low concentration of chain entanglements and indicates weak intermolecular interactions between the individual supramolecular chains.

With the objective to improve the material's mechanical properties, we employed minor amounts of lanthanide perchlorate salts, which are well known to bind three Mebip ligands,³³ as a cross-linking / branching unit in our supramolecular polymerization of **2b** and $Fe(ClO_4)_2$ (**Figure 1**). In order to generate the cross-links/branch points in a metal ion:**2b** system that was processed as described above, 9 mol % $La(ClO_4)_3$ (with respect to **2b**) in CH_3CN was added to xylylene **2b** in $CHCl_3$ (71.4 mg/mL) with the assumption of a 3:1 Mebip: La^{3+} binding motif. The further addition of 91 mol % $Fe(ClO_4)_2$ in CH_3CN resulted in an instantaneous and dramatic visual increase of the solution's viscosity, illustrating the successful linear chain growth (via 2:1 Mebip:**2b** binding) of the preformed 3:1 Mebip: La^{3+} complexes. Solution casting and slow evaporation of the solvent led to purple films, which displayed appreciable mechanical properties (**Figure 11**). The deep purple color of the material results virtually exclusively from a metal-to-ligand charge transfer (MLCT), indicative of the formation of 2:1 Mebip: Fe^{2+} complexes, as the addition of $La(ClO_4)_3$ to **2b** resulted in the formation of only near colorless solutions.^{24, 32} In addition, the PL emission associated with **2b** is fully quenched. **Figure 4** shows unequivocally that solution-processed objects from $[2b \cdot Fe(ClO_4)_2/La(ClO_4)_3]_n$ - very much in contrast to the neat xylylene **2b** and poly(2,5-dioctyloxy-*p*-xylylene)s¹⁵ of similar X_n but without Mebip endgroups - exhibit appreciable mechanical strength and flexibility.

The solid-state structure of $[2b \cdot Fe(ClO_4)_2/La(ClO_4)_3]_n$ was investigated by wide-angle X-ray diffraction (WAXD). Three distinct peaks are discernible in the diffraction pattern (**Figure 12**). The most prominent and sharpest of the reflections occurs at $2\theta = 4.6^\circ$, corresponding to a d spacing of 19.8 Å. At higher 2θ values, two broad reflections are observed with d spacings of approximately 7.7 and 4.2 Å. Considering the stark similarity of these reflections to that of 2,5-dialkyloxy(*p*-phenylene-ethynylene)s, the WAXD data suggest that the morphology of the self-assembled system is lamellar and is largely driven by side-chain packing.

Thermomechanical Properties of $[2b \cdot Fe(ClO_4)_2/La(ClO_4)_3]_n$. The mechanical and thermal properties of $[2b \cdot Fe(ClO_4)_2/La(ClO_4)_3]_n$ films were investigated in more detail by means of thermogravimetric analysis (TGA), dynamic mechanical thermoanalysis (DMTA), and modulated differential scanning calorimetry (MDSC); these experiments were all conducted under nitrogen atmosphere. TGA traces (**Figure 13**) of neat **2b** reveal an onset of significant weight loss (2%) at 354 °C, which has previously been related to the degradation of alkyl side chains.³⁴ The supramolecular polymer $[2b \cdot Fe(ClO_4)_2/La(ClO_4)_3]_n$ shows a rather similar overall thermal behavior (**Figure 13**). For the materials investigated here, however, the initial 2% weight loss was observed at a substantially lower temperature (193 °C), which we ascribe to the thermal degradation of the perchlorate counterions upon melting (vide infra).

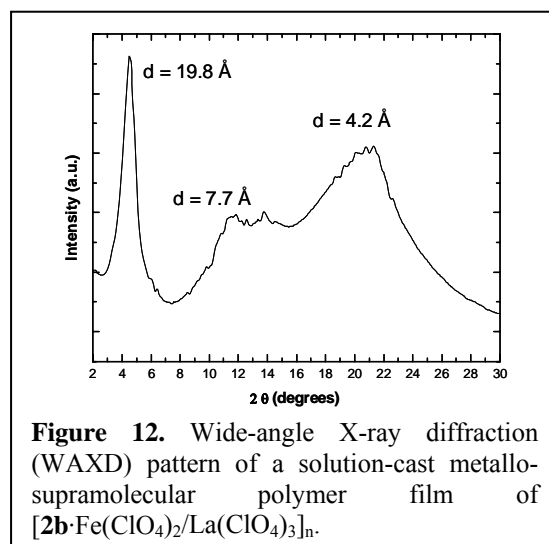


Figure 12. Wide-angle X-ray diffraction (WAXD) pattern of a solution-cast metallo-supramolecular polymer film of $[2b \cdot Fe(ClO_4)_2/La(ClO_4)_3]_n$.

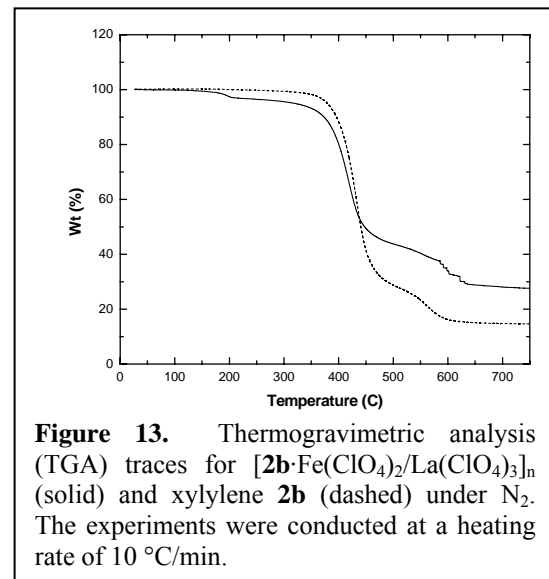
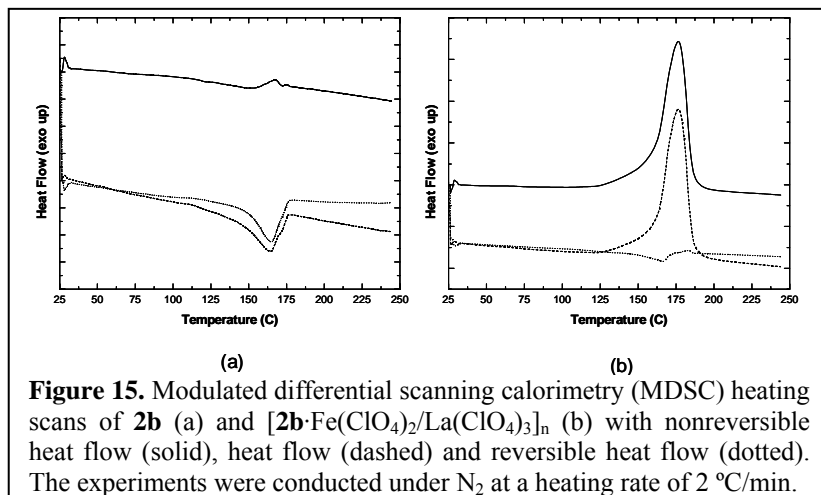
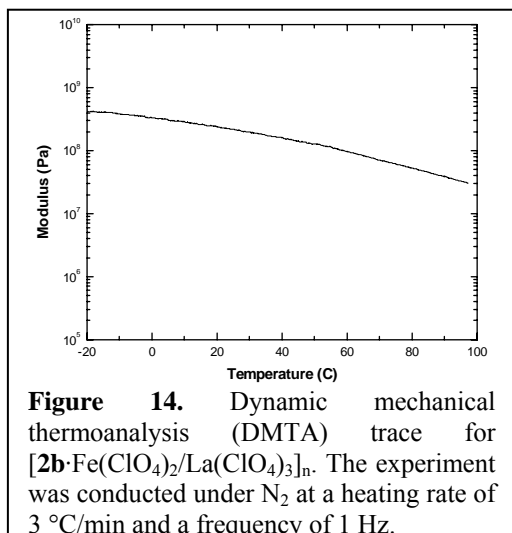


Figure 13. Thermogravimetric analysis (TGA) traces for $[2b \cdot Fe(ClO_4)_2/La(ClO_4)_3]_n$ (solid) and xylylene **2b** (dashed) under N_2 . The experiments were conducted at a heating rate of 10 °C/min.

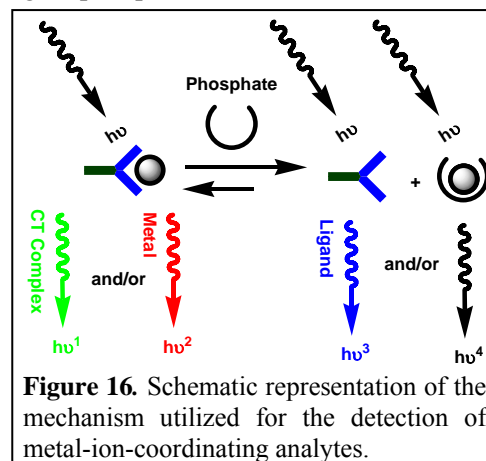


The mechanical properties of $[2\mathbf{b}\cdot\text{Fe}(\text{ClO}_4)_2/\text{La}(\text{ClO}_4)_3]_n$ were elucidated by DMTA in a temperature range of -20 to 100°C (**Figure 14**). The room-temperature modulus was determined to be 220 MPa , placing the self-assembled system in the same regime as low-density polyethylene. The modulus decreased continuously as the temperature was increased, which may be on account of progressive decomplexation of the more weakly bound lanthanide-Mebip cross-links. In order to determine the melting temperature, T_m , of both $2\mathbf{b}$ and $[2\mathbf{b}\cdot\text{Fe}(\text{ClO}_4)_2/\text{La}(\text{ClO}_4)_3]_n$, MDSC experiments were performed (**Figure 15**). The MDSC trace of neat $2\mathbf{b}$ clearly shows a reversible endotherm with maximum at 166°C corresponding to the T_m , which is virtually identical to that reported for a poly(2,5-dioctyloxy-*p*-xylylene) of similar X_n but without Mebip endgroups (170°C).¹⁵ The MDSC trace of $[2\mathbf{b}\cdot\text{Fe}(\text{ClO}_4)_2/\text{La}(\text{ClO}_4)_3]_n$ shows a largely irreversible exotherm at 176°C that we associate, by comparison with TGA data, to the degradation of the perchlorate counterions. The reversible portion of the scan shows a weak endotherm at 166°C which corresponds to melting at a temperature which is nearly identical to that of $2\mathbf{b}$. Thus, the MDSC data suggest that the melt transition of the new metallo-supramolecular PPX is largely governed by the hydrocarbon building block, and can be tailored to meet specific thermal demands by judicious design of the latter.

Metallo-Supramolecular Polymers as Organophosphate Sensors. We have shown that addition of metal ions to the highly fluorescent conjugated ditopic monomers not only results in the formation of metallo-supramolecular polymers but also has a significant effect on their fluorescent behavior. Thus we initiated a preliminary study aimed at investigating the potential of these systems as sensing materials. Our initial study focused on organophosphates, as mimics for chemical warfare agents (CWA) and aliphatic amines, but we should stress that the general concept is probably very broadly applicable. The basic mechanism proposed relies on competitive binding, in which the analyte displaces the metal bound Mebip-end capped monomer, which in turn results in a change or increase in the fluorescence of the system (**Figure 16**).

Metal complexes used as model compounds for our high-temperature work were used to demonstrate concept feasibility and explore how the structure of the ligand and the nature of the metal ion (e.g. La^{3+} , Eu^{3+} or Zn^{2+}) effect the phosphate sensing abilities of these complexes. We further studied the relationship between the electron density of the aromatic fluorescent ligand/chromophore and the optical response of the sensor complex and the influence of the different binding capabilities of selected metal ions (e.g. lanthanide vs. Zn^{2+} ions) on the selectivity of the sensor complexes.

Ideally, the sensor response should be easy to read and involve a marked visual change. Most metal ions, e.g. Zn^{2+} or La^{3+} , do not lend themselves to metal-based emission. In these cases, ligand-based fluorescence may be quenched or shifted to a different wavelength upon complexation. The inverse process, which is exploited here as the sensory response, occurs upon exposure to an analyte that competitively displaces the ligand/chromophore from the metal ion. Similarly, the concept can also utilize the metal-based emission of certain lanthanide complexes, which display narrow emission bands, intense fluorescence and long excited-state lifetimes.³⁵ For example, Eu^{3+} complexes exhibit intense luminescence in the presence of an appropriate, UV-light-absorbing ligand, via the so-called “antenna effect”.³⁶ This process involves optical absorption by the ligand, followed by ligand-to-metal energy transfer and results in metal-based fluorescence. Any analyte, which can act as a competitive binder for the Eu^{3+} , can “switch-off” the Eu^{3+} -based emission and potentially

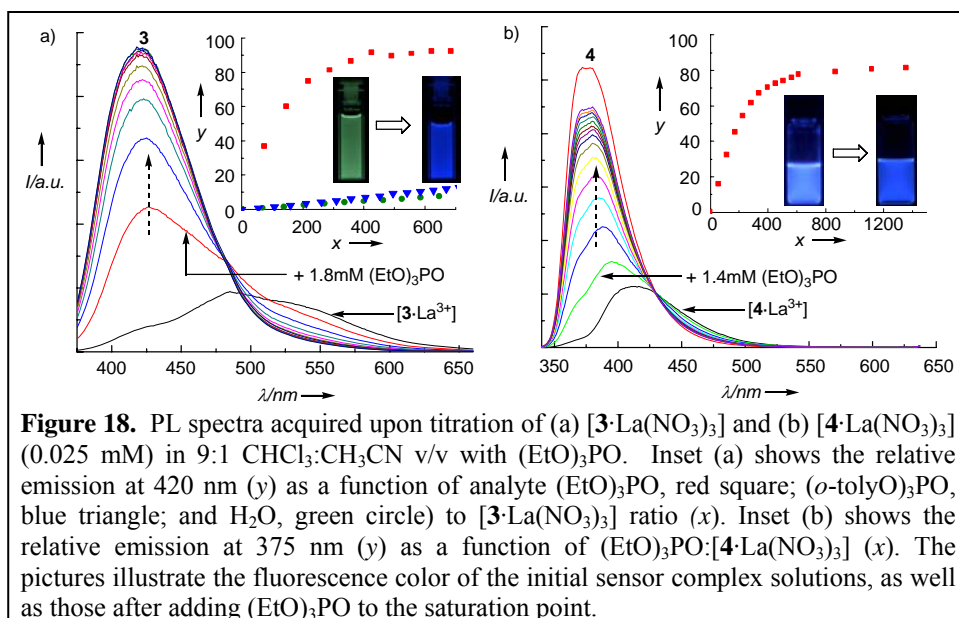
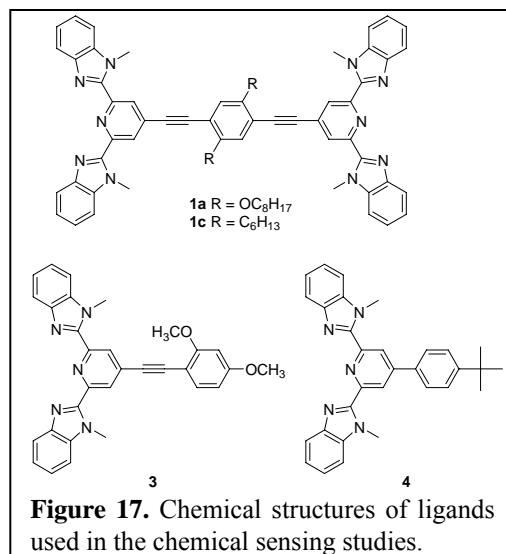


restore the emission of the “free” ligand. Taking advantage of both these processes and exploiting the known binding affinity of organophosphates to lanthanide ions,^{35c} we started to investigate a sensor platform that combines high selectivity and sensitivity with ease of signal transduction. The approach relies on the fact that Mebip ligands such as **1a**, **1c**, **3** and **4** (**Figure 17**) are highly fluorescent and that these ligands/chromophores either show a chromogenic response upon metal (de)complexation or act as “antenna” for ions such as Eu^{3+} or Tb^{3+} .³⁷ The magnitude of the color shift of ligand-based emission upon metal ion (de)complexation can be tuned by the electron-density of the aromatic ligand. Mixing and matching consciously designed ligands and carefully selected metal ions allows the formation of sensor complexes which can exhibit different selectivity and optical response.

The organophosphate sensing capability of complexes **1a**, **1c**, **3** and **4** was explored with the CWA mimic triethylphosphate. In addition, tri-*o*-tolylphosphate was employed to investigate the selectivity of the phosphate sensing. The phosphates were titrated into dilute $\text{CHCl}_3\text{:CH}_3\text{CN}$ solutions of each complex. **Figure 18** shows data for the response of $[\mathbf{3}\cdot\text{La}(\text{NO}_3)_3]$ and $[\mathbf{4}\cdot\text{La}(\text{NO}_3)_3]$ to selected analytes. In the case of the aliphatic phosphate, an instantaneous blue shift of the emission spectra and increase of the fluorescence intensities are observed, indicating the release of “free” ligand (**Figure 18**) and consistent with the phosphate binding to La^{3+} . Plotting the relative fluorescence intensity as a function of analyte concentration yields a sensory response for each complex (**Figure 18, insets**). The importance of bestowing the ligand with electron donating substituents is readily evident, as a visible fluorescence color change was observed for $[\mathbf{3}\cdot\text{La}^{3+}]$ whereas the sensory response of $[\mathbf{4}\cdot\text{La}^{3+}]$ could only be monitored spectroscopically. Interestingly, the addition of the bulky aromatic phosphate, (*o*-tolylO)₃PO, yielded only very small responses when added to $[\mathbf{3}\cdot\text{La}^{3+}]$ (**Figure 18a**), indicating the virtual absence of free ligand and pointing to very weak competitive binding. A very similar response was observed for water at comparably high concentrations, demonstrating that this sensor system shows excellent selectivity for the detection of alkyl phosphates over bulky aromatic phosphates and water.

Having established the high selectivity of these Mebip· La^{3+} complexes for trialkylphosphate over the bulky triarylphosphate and water, La^{3+} was substituted with Eu^{3+} and Zn^{2+} to further explore the influence of different metal ions on the sensory capacity of the resulting complexes. The $[\mathbf{3}\cdot\text{Zn}^{2+}]$ complex fluoresces yellow and displays an even larger bathochromic shift of the emission band ($\Delta\lambda_{\text{max}} = 150 \text{ nm}$) than $[\mathbf{3}\cdot\text{La}^{3+}]$. By contrast, the $[\mathbf{3}\cdot\text{Eu}^{3+}]$ complex displays emission characteristics that are dominated by a red, metal-based fluorescence while the ligand-based emission is fully suppressed. The sensory response of $[\mathbf{3}\cdot\text{Eu}^{3+}]$, was observed to behave in a similar manner to that of $[\mathbf{3}\cdot\text{La}^{3+}]$ indicating that the binding of La^{3+} and Eu^{3+} to **3** is comparable (**Figure 19a**). However, the visual effect is much more pronounced in the case of the $[\mathbf{3}\cdot\text{Eu}^{3+}]$ complex on account of the large color difference of the intense Eu^{3+} -based (red) and free ligand (blue) emission.

To determine the sensitivity of these new sensor complexes, triethylphosphate titrations were conducted with $[\mathbf{4}\cdot\text{Eu}^{3+}]$ with smaller aliquots of the analyte. The experiments yielded a spectroscopically observable increase of the fluorescence intensity corresponding to free ligand at analyte concentrations of ca. 20 μM . In contrast to its lanthanide counterparts, $[\mathbf{3}\cdot\text{Zn}^{2+}]$ showed no increase of “free” ligand-fluorescence intensity upon addition of even large amounts (19 mM) of $(\text{EtO})_3\text{PO}$ (**Figure 19a**). The absence of a response for $[\mathbf{3}\cdot\text{Zn}^{2+}]$ illustrates the stronger binding of Mebip to Zn^{2+} ions



compared to Ln^{3+} ions and/or a preference of the phosphate for interacting with Ln^{3+} ions, clearly demonstrating the importance of tailoring the strength of the metal-ligand interaction to an appropriate level.

One important aspect in designing effective organophosphate sensors is to impart a high degree of analyte specificity, which is necessary to avoid false positive readings. To determine the extent to which our complexes respond to various common organic species, 25 μM solutions of $[\mathbf{4}\cdot\text{La}^{3+}]$ and $[\mathbf{4}\cdot\text{Zn}^{2+}]$ were exposed to a variety of compounds (2.5 mM). As can be seen from the data compiled in **Figure 19b** both complexes show effectively no response to ketones, esters, organic acids, ethers, alcohols, water and bulky aromatic phosphates demonstrating a high degree of selectivity. Apart from the trialkylphosphate, the only other investigated analyte that elicited a response was triethylamine. While

$[\mathbf{4}\cdot\text{La}^{3+}]$ shows a response to both trialkylphosphate and triethylamine, $[\mathbf{3}\cdot\text{Zn}^{2+}]$ and $[\mathbf{4}\cdot\text{Zn}^{2+}]$ do not report the presence of aliphatic phosphates but do respond to amines ($[\mathbf{4}\cdot\text{Eu}^{3+}]$ actually responds to nano-molar concentrations of triethylamine, demonstrating the potentially high sensitivity of this approach). Thus the use of different combinations of metal ions and Mebip ligands allows one to differentiate between aliphatic phosphates and amines. This point is illustrated clearly by the sensor array shown in **Figure 20a**. The array demonstrates the ability to detect the presence of aliphatic over bulky aromatic phosphates, and exclude amine-related false-positive readings.

In practical devices, the detection of analytes vapors can be accomplished by a variety of methods. For example, the sensor complexes may be dissolved and the sensor solutions are brought in contact with the vapor (e.g. a CWA in air); this can occur in a “passive” mode in which the solution is simply exposed to the analyte vapor, as well as in “active” schemes in which a stream of the vapor is guided through the sensor solution. The same modes apply to solid-state sensors, which are generally simpler to handle and operate, but can have a longer response time, especially if their surface area is low. First experiments to probe the usefulness of the proposed sensor scheme in the solid state, involved hydrophobic silica particles that were treated with a solution of $[\mathbf{4}\cdot\text{Eu}^{3+}]$ yielding (after drying) a pink-fluorescent powder (**Figure 20b**). Upon exposure to $(\text{EtO})_3\text{PO}$ vapor the fluorescence color of powder changed slowly (on account of the low vapor pressure of this analyte; this was confirmed by the fact that exposure of the solid-state sensor to $(\text{EtO})_3\text{PO}$ in liquid form resulted in an instantaneous response) from pink to blue (**Figure 20c**), indicative of the decomplexation of $[\mathbf{4}\cdot\text{Eu}^{3+}]$ and the formation of “free” ligand **4**.

Summary

In order to develop thermally stable and easily processable poly(*p*-xylylene) derivatives, we utilized metal ion mediated self-assembly polymerization. We successfully developed a synthetic framework for the synthesis of PPE and PPX-based ditopic ligands. We demonstrated that the supramolecular metallopolymerization of both types of macromonomers with a variety of metal ions leads to the formation of polymer materials that display very good mechanical properties and are easy-to-process. Our PPE-based supramolecular metallopolymers with either Zn^{2+} or Fe^{2+} ions are one of the first (if not the first) examples of a conjugated supramolecular material that combines the functionality of organic semiconductors with mechanical properties typical of polymer materials. Our preliminary studies on the optical properties of these materials have only scratched the surface of the potential that such inorganic/organic hybrid polymers can offer. The design concept is versatile and readily adoptable to other conjugated cores, ligands and metal ions. The already very high number of citations of our work supported by this grant indicates the significant impact of our findings in this field.

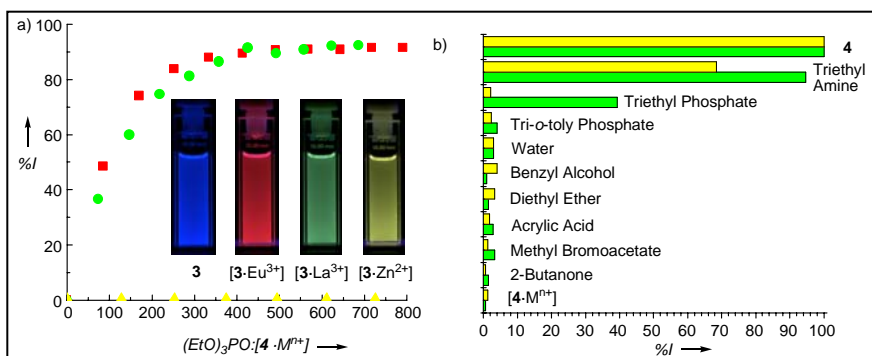


Figure 19. (a) Relative emission at 420 nm as a function of the ratio of $(\text{EtO})_3\text{PO}$ to the 1:1 metal/ligand complexes $[\mathbf{3}\cdot\text{MX}_n]$ (0.025 mM, $\text{M} = \text{Eu}^{3+}$, La^{3+} and Zn^{2+}) in 9:1 $\text{CHCl}_3:\text{CH}_3\text{CN}$ v/v. (b) Relative PL intensity (relative to intensity of free ligand) of solutions of $[\mathbf{4}\cdot\text{La}(\text{NO}_3)_3]$ and $[\mathbf{4}\cdot\text{Zn}(\text{ClO}_4)_2]$ (25 μM in 9:1 $\text{CHCl}_3:\text{CH}_3\text{CN}$ v/v) upon exposure to organic compounds (2.5 mM).

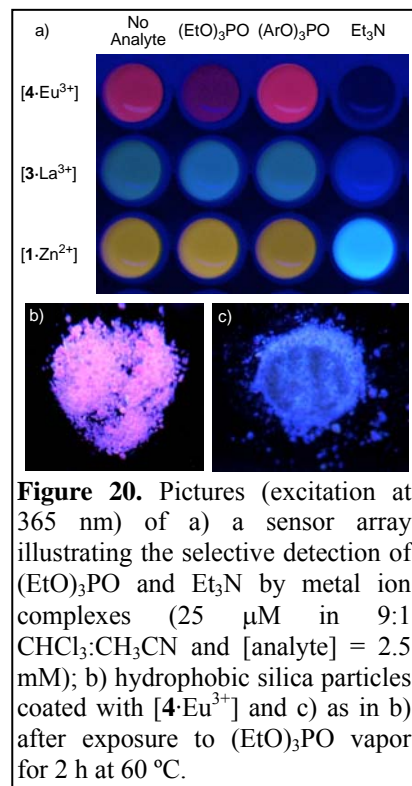


Figure 20. Pictures (excitation at 365 nm) of a) a sensor array illustrating the selective detection of $(\text{EtO})_3\text{PO}$ and Et_3N by metal ion complexes (25 μM in 9:1 $\text{CHCl}_3:\text{CH}_3\text{CN}$ and $[\text{analyte}] = 2.5$ mM); b) hydrophobic silica particles coated with $[\mathbf{4}\cdot\text{Eu}^{3+}]$ and c) as in b) after exposure to $(\text{EtO})_3\text{PO}$ vapor for 2 h at 60 $^\circ\text{C}$.

We further demonstrated that the supramolecular metallopolymerization of PPX-based ligand end-capped macromolecules with a mixture of Fe^{2+} and La^{3+} can be employed to produce materials that combine good mechanical characteristics with a solution-processing capability that can not be attained with conventional PPX derivatives. The introduction of La^{3+} which can bind three ligands and act as a cross-linking / branching unit was shown to be a most important design tool. In the case of the supramolecular PPX polymers investigated here, this concept proved to be key in creating materials with good mechanical characteristics. While further refinements are needed, the first generation of supramolecular PPX polymers developed and investigated under this grant clearly opens the door to processable materials with good stability at high temperatures.

We further exploited the chemistry and model compounds synthesized in this project to develop a modular sensory system which utilizes a multi-metal/multi-ligand based approach. The judicious design of fluorescent ligands and the careful selection of metal/ligand combinations allowed us to create a very simple system that appears to allow the selective detection of aliphatic organophosphates with good sensitivity. By tailoring the nature of the metal-ligand interactions, it is possible to further enhance the sensitivity of these systems on the one hand, and tailor their selectivity towards different analytes on the other.

(5) "Technology transfer" (any specific interactions or developments which would constitute technology transfer of the research results). None

(6) Other info:

Total number of publications submitted or published in refereed journals: 5

Number of publications in Science and Nature: 0

Number of publications with DoD personnel as co-author: 0

Number of presentations with DoD personnel as co-author: 0

Number of awards (not grants/contracts, but professional society, etc.) for PI and co-PIs: 0

Total number of invention disclosures, patents applied for and awarded: 0

Transfer of materials or techniques to Army, DoD, or industry. 0

Number of visits to DoD labs including lab name: 1, Army Research Laboratory, Aberdeen Proving Ground, MD

Is there any other brief info that would help me sell the value of your program to the Army?

This grant has enabled us to establish the scientific basis for a new modular concept that serves as the basis for the development of new polymers which combine ease of processing with desirable materials properties. Indications for the high scientific impact of the research are (i) the publication of manuscripts in high impact international journals, (ii) the fact that one of the papers (Chem. Comm.) was flagged by the journal as one of its "most accessed articles", and (iii) the fact that all manuscripts are (despite their recent publication) heavily cited (ca. 9 hits/paper/year, much above the Journals' impact factors). Exploitation of the new approach in the area of high-temperature is continuing through a new grant funded by the ARO.

In addition, exploratory work under this ARO grant allowed to PIs to elucidate other ways the new materials could be of use to Army. This led to the discovery of (a broadly applicable concept for a) new class of chemical warfare agent sensors. This was such a success it led to one publication and to a new grant being submitted in response to the ARO BAA W911NF-06-R-0005 "Basic Research Program in Chemical, Biological, Radiological, and Nuclear Defense of the Joint Science and Technology Office Physical Science and Technology Division Defense Threat Reduction Agency".

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